

Suzuki – Miyaura cross-coupling reaction of aryl bromides catalyzed by a palladium(II) complex encaged in Y zeolite

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Abstract

An efficient approach for the catalytic synthesis of biaryl compounds via the Suzuki-Miyaura cross-coupling reaction of aryl bromides with arylboronic acids is described using a palladium-1,10-phenanthroline complex encaged in Y zeolite (PdCl₂(phen)@Y) as the catalyst. In aqueous solution, PdCl₂(phen)@Y exhibited remarkable activity, and only 0.5 mol% palladium loading was required to achieve good to excellent yields of biaryl products. The catalyst can be easily separated by a simple centrifugation process and used up to five times with only slight loss of activity. The salient features of this protocol are the simplicity in handling of catalyst, good functional group tolerance, high catalytic activity, negligible palladium leaching and effective catalyst recyclability.

Keywords

Palladium, heterogeneous catalysis, Suzuki–Miyaura cross-coupling, aqueous media.

1. Introduction

Water is an ideal solvent for chemical transformations, since it offers the advantages of nontoxicity, nonflammability and low cost [1,2]. Meanwhile, separation and recycling of homogeneous catalysts is considered a key green chemistry research area [3,4]. From the standpoint of environmentally benign organic synthesis, the development of highly efficient immobilized catalysts and the use of water instead of organic compounds as solvent are of great interest to chemists [5-7].

In recent years, palladium-catalyzed Suzuki-Miyaura coupling reaction [8,9] of aryl halides is one of the most efficient methods for the construction of biaryls or substituted aromatic moieties in organic synthesis. Thus far, a considerable number of highly active palladium complexes have been developed for Suzuki-Miyaura coupling reactions of organic halides, as well as these reactions performed in water [10]. However, separation, recovery and recycling of the expensive metal and ligands from the final reaction mixture is the problem to be addressed. In this regard, researchers have immobilized palladium complexes on various supports such as carbon [11], magnetic materials [12], silica [13], hydroxyapatite [14], zeolites [15], MOFs [16] and organic polymers [17] to create heterogeneous catalysts, despite the fact that a substantial decrease of catalytic activity is frequently observed in the heterogeneous systems. In the terms of both academia and industry, developing more active heterogeneous catalytic systems is imperative and merits further study.

In order to extend the application of the active PdCl₂(phen)@Y heterogeneous catalyst [18-20], in this paper, we wish to explore the Suzuki-Miyaura cross-coupling of aryl bromides in aqueous media using PdCl₂(phen)@Y as a catalyst.

2. Experimental

2.1 Materials

NaY zeolite was purchased from Nanjing Nanda Surface and Interface Chemical Engineering and Technological Research Center Co. Ltd., China. 1,10-phenanthroline monohydrate (phen•H₂O) was purchased from Alfa Aesar. Palladium nitrate dihydrate, palladium chloride, potassium carbonate, aryl bromides, arylboronic acids and ethanol were of analytical reagent grade and commercially available. NaY zeolites were calcined at 350 °C for 3 h before used.

2.2 Preparation of catalysts

The preparation procedures and physico-chemical measurements of heterogeneous catalyst PdCl₂(phen)@Y can be found in our previous research [18-20]. The loaded Pd content was indirectly calculated according to AAS analysis of the residual Pd in the filtrate. The Pd content of PdCl₂(phen)@Y was 2.1 wt%.

2.3 Catalytic activity test and recycling

All reactions were conducted in a 10 mL tubular flask equipped with a magnetic stirring bar. In a typical procedure, 0.5 mol% PdCl₂(phen)@Y, 0.5 mmol bromobenzene, 0.75 mmol phenylboronic acid and 1 mmol K₃PO₄·3H₂O were added to 2 ml solvent (EtOH : H₂O = 3 : 2 v/v). The mixture was stirred at 60 °C in air for 2 h. The product was obtained by preparative TLC using petroleum ether (bp 60-90 °C) as the eluting solvent. All the synthesized biaryl compounds are known products, and we have reported previously [21].

For the recycling experiments, 0.5 mol% PdCl₂(phen)@Y, 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 2 mmol K₃PO₄·3H₂O, and 40 mg naphthalene (as internal standard for GC analysis) were added to 2 ml solvent (EtOH : H₂O = 3 : 2 v/v). The reaction was carried out at 60 °C in air for 2 h. Then the mixture was separated quickly by centrifugation. The clear supernatant was analyzed by GC. The obtained catalyst was washed by distilled water and ethanol, dried under vacuum and used in the next run.

3. Results and discussion

3.1 Catalytic activity

To test the catalytic activity of PdCl₂(phen)@Y in the Suzuki–Miyaura cross-coupling reaction, coupling reaction of bromobenzene and phenylboronic acid was chosen as a model reaction. The reaction was simply performed under air pressure, and the results are shown in Table 1. Previous studies have suggested that solvents and bases had remarkable influences on the activity of the Suzuki reaction [22,23]. Hence, the effect of solvent was examined firstly (Table 1, entries 1-3). The results showed that 60% aqueous ethanol was the best choice for the reaction medium, which gave a 83% yield of biphenyl (Table 1, entry 3). To clarify the effect of base in this model reaction, several common and cheap inorganic bases were then tested (Table 1, entries 3-5). Notably, K₃PO₄·3H₂O afforded the highest yield of biphenyl, and almost quantitative biphenyl yield was obtained (Table 1, entry 5). With these results in hand, we tried to lower the catalyst usage. When 0.3 mol% of PdCl₂(phen)@Y was used, the reaction proceeded also well, but the yield obtained was slightly inferior compared with that of 0.5 mol% catalyst (Table 1, entry 6).

Table 1. Effect of solvent and base^a

Entry	Solvent	Base	Yields (%) ^b
1	EtOH–H ₂ O (1 : 2)	K ₂ CO ₃	38
2	EtOH–H ₂ O (1 : 1)	K ₂ CO ₃	66
3	EtOH–H ₂ O (3 : 2)	K ₂ CO ₃	83
4	EtOH–H ₂ O (3 : 2)	Na ₂ CO ₃	77
5	EtOH–H ₂ O (3 : 2)	K ₃ PO ₄ ·3H ₂ O	99
6 ^c	EtOH–H ₂ O (3 : 2)	K ₃ PO ₄ ·3H ₂ O	94

^a Reaction conditions: PdCl₂(phen)@Y (0.5 mol%), bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1 mmol), solvent (2 mL), 60 °C, 2 h, stirring speed (500 rpm).

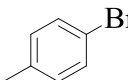
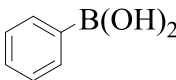
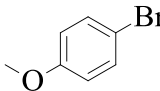
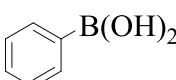
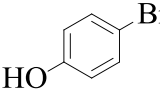
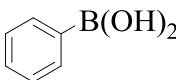
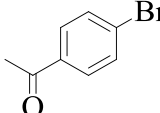
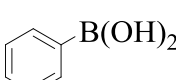
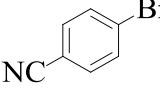
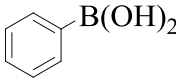

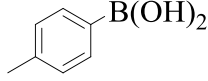

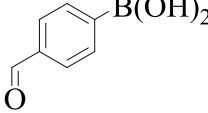
^b GC yields.

^c PdCl₂(phen)@Y (0.3 mol%).

3.2 Substrate scope

With the optimized conditions in hand, we turned our focus to the scope and limitations of the system (Table 2). Firstly, we extended the scope of this reaction to a wide range of aryl bromides with phenylboronic acid (Table 2, entries 1-5). Various electron-donating and electron-withdrawing groups on the aryl bromides such as *p*-Me, *p*-OMe, *p*-OH, *p*-COCH₃ and *p*-CN were also well tolerated and gave the desired products in good to excellent yields (Table 2, entries 1-5). Next, the Suzuki-Miyaura cross-coupling reaction of bromobenzene with different arylboronic acids were carried out, and they gave the biaryl compounds in excellent yields (Table 2, entries 6 and 7).

Table 2. effect of solvent and base^a

Entry	Ar-Br	Ar-B(OH) ₂	Yields (%) ^b
1			94
2			92
3			95
4			90
5			97
6			95
7			93

^a Reaction conditions: PdCl₂(phen)@Y (0.5 mol%), aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), K₃PO₄·3H₂O (1 mmol), 2 ml of EtOH : H₂O (3 : 2 v/v), 60 °C, 2 h, stirring speed (500 rpm).

^b Isolated yields.

3.3 The recycling of the catalyst

For a heterogeneous catalytic system, recovery, reuse of the catalyst and the amount of palladium leaching are also crucial for an excellent heterogeneous catalyst. Under the optimized conditions, recycling capacity was evaluated for the Suzuki-Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid (Fig. 1). after every cycle, the catalyst was separated by simple centrifugation. The results suggested that PdCl₂(phen)@Y exhibited good reusability and could be used five cycles with only a slight decrease of catalytic activity. ICP-AES analysis was carried out using the filtrate after each run, and the palladium leaching was found to be less than 0.5 ppm in each run.

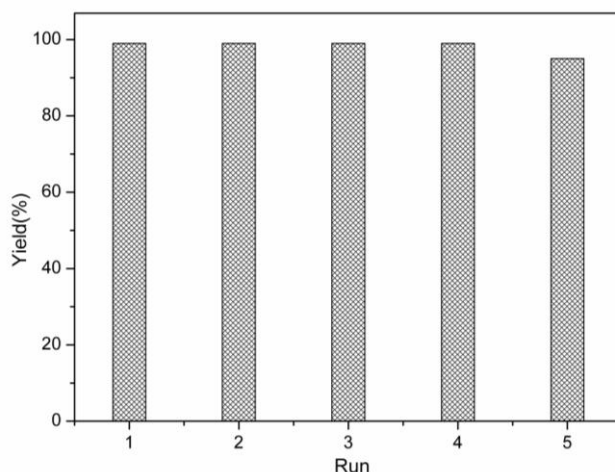


Fig. 1 Recycling test of PdCl₂(phen)@Y in the Suzuki-Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid

4. Conclusion

In conclusion, an efficient protocol for the Suzuki-Miyaura cross-coupling reaction of aryl bromides with arylboronic acids using PdCl₂(phen)@Y as a highly active and reusable catalyst has been developed. In an aqueous solution, a palladium catalyst loading as low as 0.5 mol% was sufficient for moderate to excellent yields of the corresponding biaryls. The catalyst can be used five times with a slight decrease in activity. The easy availability and simple separation make such supported palladium catalyst an interesting alternative to the homogeneous catalysts in Suzuki-Miyaura cross-coupling reactions.

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